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No. Sho 60[1985]-120750

THIXOTROPIC POLYURETHANE COMPOSITIONS

Noriaki Shin et al.

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THIXOTROPIC POLYURETHANE COMPOSITIONS

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Applicant:	Yokohama Rubber Co., Ltd.

[There are no amendments to this invention.]

Claim

Thixotropic polyurethane compositions, characterized by blending 0.1-20 parts by weight of urea derivatives and 0.1-50 parts by weight of colloidal silica with 100 parts by weight of polyurethanes.

### Detailed description of the invention

The present invention pertains to thixotropic polyurethane compositions. More precisely it pertains to thixotropic polyurethane compositions which impart thixotropy without reducing storage stability and workability such as mixing and application by blending specific amounts of urea derivatives and colloidal silica with polyurethanes.

Polyurethanes are excellent in rubber elasticity, weather resistance, wear resistance, etc., therefore they are widely used as coating materials for paper, cloth, elastomers, etc. and as building materials such as adhesives, floor materials, wall materials, etc.

For the application of the polyurethanes, generally speaking, paste-like or liquid compositions made of liquid or solution polyurethane prepolymers are used, and gap fillers such as talc, carbon black, etc., plasticizers, adhesion-imparting agents, hardening catalysts, coloring materials, etc. are blended. Depending on the hardening method used, polyurethanes can be classified into one-component polyurethanes in which the terminals of the urethane prepolymer have isocyanate groups with hardening occurring by the moisture in air and two-component polyurethanes in which the hardening is carried out by polyols. Depending on the use of polyurethanes, from the viewpoint of application very often they (polyurethanes) exhibit thixotropy. For example, if polyurethanes are used as a coating material or sealant and coated or sealed on a vertical surface, because it takes time to handle a brush and spatula, sagging can hardly occur and the finish is beautiful. And when they are used as an adhesive or a coating material and coated on porous paper and cloth, a little blotting occurs on the paper and cloth so the coating process is easy which is advantageous.

As a method for imparting thixotropy to polyurethanes and preventing sagging at the time of their application such as for coating or sealing, heretofore the use of anti-sagging agents such as colloidal silica and bentonite has been proposed. With increase in the amount of the anti-sagging agent such as colloidal silica, the thixotropy is improved and the sagging is suppressed but the apparent viscosity of the polyurethanes becomes remarkably high so the workability such as in mixing, application, etc. degrades, and after hardening, physical properties such as the hardness and modulus increase and the elongation and adhesion properties become poor, therefore they cannot satisfy the required properties for construction materials such as sealants, adhesives, coating materials, etc.

Thus methods for imparting thixotropy without impairing other properties have been proposed. For example,

① Polyurethane compositions prepared by mixing a specific amount of polyethylene glycol or its derivatives and colloidal silica with polyurethanes (Japanese Kokoku Patent No. Sho 45[1970]-41110)

② Polyurethane compositions prepared by blending inorganic fillers, polyoxyalkylene, etc. with liquid polyurethanes having terminal groups (Japanese Kokoku Patent No. Sho 47[1972]-7632).

③ Methods for manufacturing urethane sealants by combination of specific anti-sagging agents, such as sulfoxides, with polyurethanes (Japanese Kokoku Patent No. Sho 49[1974]-27418), etc.

However, even these methods have not yet been able to impart sufficient thixotropy, and the thixotropy changes during the storage and the apparent viscosity increases; therefore the workability at the time of mixing and application becomes worse, and this problem has not yet been sufficiently solved.

The present invention was formulated for solving such technological drawbacks and its object is to provide thixotropic polyurethane compositions with excellent heat resistance, weather resistance, and wear resistance without reducing their storage stability and workability such as mixing, application, etc. by imparting sufficient thixotropy to the polyurethane compositions, and especially to utilize them as sealants, gap fillers, adhesives, etc.

The present inventors carried out an extensive study for attaining the above-mentioned object and as a result it was found that by dispersing a specific amount of colloidal silica and urea derivatives in polyurethanes, sufficient thixotropy was imparted and the workability at the time of mixing and application which are other properties required for polyurethanes could be maintained sufficiently, and thereby they attained the present invention.

That is, the present invention provides thixotropic polyurethane compositions which are characterized by blending 0.1-20 parts by weight of urea derivatives and 0.1-50 parts by weight of colloidal silica with 100 parts by weight of polyurethanes (polyurethane prepolymer).

For the polyurethanes used in the present invention, in case of one-component polyurethanes, isocyanate group-terminated polyurethane prepolymers can be used. The prepolymers can be prepared, for example, by the reaction of polyisocyanates with polyether polyols such as polyoxypropylenediol or triol or others such as hydroxy group-terminated polyols with a molecular weight of 1000 - 10000. For the polyisocyanates, one or a mixture of tolylene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI), or their modified compounds can be used. In case of one-component polyurethanes, the terminal isocyanate groups of the above-mentioned prepolymers react with atmospheric moisture and macromolecules or network-like molecules for as the main structure of the polyurethanes which are characterized by having elasticity.

It is common for a polymer which forms the base of a two-component polyurethane to contain an isocyanate-terminated prepolymer similar to the above-mentioned one-component polyurethane as a constituent and a hydroxy group-terminated polyol with an average molecular

weight of 1000-5000 as another constituent. For the polyol, polyoxypropylenediol and polyoxypropylenetriol or their copolymers are often used with ethylene oxide, however, other polyols may be used also. For a two-component polyurethane, the prepolymer constituent is mixed with the polyol constituent immediately prior to application (such as for coating, sealing, etc.). The reaction is mainly the linkage, that is, urethane linkage, of the terminal groups of the two constituents, and hardening can occur without water.

These polyurethanes are originally liquid or become liquid after dissolving in a solvent. Examples of solvents used include esters such as ethyl acetate, ketones such as methyl ethyl ketone, and aromatic hydrocarbons such as toluene, etc.

Examples of urea derivatives which can be blended in the present invention include tetramethyl urea, tetraethyl urea, 1,3-dimethyl-2-imidazolidone, etc. and compounds with a molecular weight less than 1000 per urea group are preferable. The amount of urea derivative to be blended is 0.1-20 parts by weight, preferably 0.5-10 parts by weight based on 100 parts by weight of polyurethane. When it is less than 0.1 part by weight, the objective thixotropy cannot be obtained so prevention of sagging is insufficient, whereas when it is greater than 20 parts by weight, the storage stability and workability become poor.

A commercially available colloidal silica can be used for blending in the present invention. For example, Aerosil, etc. can be a representative. The amount of colloidal silica to be blended is 0.1-50 parts by weight, preferably 1-15 parts by weight based on 100 parts by weight of polyurethane. When it is less than 0.1 part by weight, the thixotropy and prevention of sagging are insufficient, whereas when it is greater than 50 parts by weight, the storage stability and workability become poor.

In the present invention, by joint blending urea derivatives and colloidal silica with polyurethanes, the hydrogen bonding of the silanol groups of the colloidal silica is further accelerated and a continuous structure is formed. The structure can be destroyed easily by a weak external force and the viscosity can drop temporarily, however, when the external force is removed a continuous structure can reappear. Thus the flowability of the polyurethane compositions of the present invention at the time of mixing and application is good so that a desired pattern can be coated on desired areas and at the finish of application, apparent viscosity is high so sagging can be suppressed.

In the polyurethane compositions of the present invention, in addition to these essential constituents, if necessary a suitable amount of fillers, plasticizers, curing promoters, agents for imparting adhesion, curing catalysts, coloring agents, etc. can be blended.

In the following, application examples and comparative examples will be used to explain the present invention in more detail.

### Application Examples 1 - 3 and Comparative Example 1

56 parts by weight of polyoxypropylenetriol with a molecular weight 5000, 44 parts by weight of polyoxypropylene glycol with a molecular weight 2000, and 20 parts by weight of dioctyl phthalate were put in a reactor, and after dehydration at 100°C under reduced pressure, cooled to 80°C under a nitrogen atmosphere. While stirring, 20 parts by weight of 4,4'-diphenylmethane diisocyanate (MDI) were added and reaction was carried out until the amount of free isocyanate was 2.54 % to prepare a urethane prepolymer.

The thus obtained urethane prepolymer, an inorganic filler, and a plasticizer with the blending ratios shown in Table 1 were put in a stirring machine, in which dry nitrogen gas was enclosed, and stirring-kneading was carried out at room temperature to give a paste-like polyurethane composition.

A slump test of the polyurethane composition was carried out using JIS A 5758 1979 sealing material slump test for construction, and 0 mm up to 1 mm was regarded as having thixotropy, whereas that greater than 1 mm was regarded as having no thixotropy.

The results of the slump test and the amount of each blending agent are shown in Table 1.

Table 1

①		④	⑧	⑨		
②	配 合		比 例 1	実 施 例 1	実 施 例 2	実 施 例 3
③	ポリウレタン樹脂		100	100	100	100
③	可 塑 剤 * 1	80	60	60	60	60
⑤	充 填 剤 * 2	50	50	50	50	50
⑤	コロイド状シリカ * 3	10	10	10	10	10
⑥	尿素誘導体-1 * 4	-	3	-	-	-
⑥	尿素誘導体-2 * 5	-	-	3	-	-
⑥	尿素誘導体-3 * 6	-	-	-	3	-
⑦	測 定 性		無	有	有	有

\*1: Dioctyl phthalate, \*2: Calcium carbonate, \*3: Aerosil, \*4: Tetramethyl urea, \*5: Tetraethyl urea, \*6: 1,3-Dimethyl-2-imidazolinone.

Key:	1	Blending
	2	Polyurethane
	3	Plasticizer
	4	Filler
	5	Colloidal silica
	6	Urea derivative
	7	Thixotropy
	8	Comparative Example 1
	9	Application Example

From the results of Table 1 it is clear that the thixotropy of polyurethane compositions (Application Examples 1-3) prepared by blending both urea derivatives and colloidal silica with polyurethane was better than that of a polyurethane composition (Comparative Example 1) obtained by blending only colloidal silica with polyurethane.

#### Application Examples 4 - 6 and Comparative Example 2

The urethane prepolymer obtained in Application Example 1, inorganic fillers, and plasticizers with the blending ratios shown in Table 2 were put in a stirring machine enclosed with dry nitrogen gas and stirring kneading was carried out at room temperature to give paste-like polyurethane compositions.

Slump testing of the polyurethane compositions was carried out as in Application Example 1 and the results along with the amount of each blending agent are shown in Table 2.

Table 2

		⑨			
②	①	比較例 2	実施例 4	実施例 5	実施例 6
	ポリウレタン樹脂	100	100	100	100
	可塑剤 * 1	60	60	60	60
	充填剤 * 2	50	50	50	50
	コロイド状シリカ * 3	—	8	15	10
⑥	⑤	—	—	—	—
	④	—	—	—	—
⑦	③	—	—	—	—
	②	—	—	—	—
⑧	①	—	—	—	—
	②	—	—	—	—
⑩	③	—	—	—	—
	④	—	—	—	—
⑪	⑤	—	—	—	—
	⑥	—	—	—	—
⑫	⑦	—	—	—	—
	⑧	—	—	—	—
⑬	⑨	—	—	—	—
	⑩	—	—	—	—
⑭	⑪	—	—	—	—
	⑫	—	—	—	—
⑮	⑬	—	—	—	—
	⑭	—	—	—	—
⑯	⑮	—	—	—	—
	⑯	—	—	—	—
⑰	⑰	—	—	—	—
	⑱	—	—	—	—
⑱	⑲	—	—	—	—
	⑳	—	—	—	—
㉑	㉑	—	—	—	—
	㉒	—	—	—	—
㉒	㉒	—	—	—	—
	㉓	—	—	—	—
㉓	㉓	—	—	—	—
	㉔	—	—	—	—
㉔	㉔	—	—	—	—
	㉕	—	—	—	—
㉕	㉕	—	—	—	—
	㉖	—	—	—	—
㉖	㉖	—	—	—	—
	㉗	—	—	—	—
㉗	㉗	—	—	—	—
	㉘	—	—	—	—
㉘	㉘	—	—	—	—
	㉙	—	—	—	—
㉙	㉙	—	—	—	—
	㉚	—	—	—	—
㉚	㉚	—	—	—	—
	㉛	—	—	—	—
㉛	㉛	—	—	—	—
	㉜	—	—	—	—
㉜	㉜	—	—	—	—
	㉝	—	—	—	—
㉝	㉝	—	—	—	—
	㉞	—	—	—	—
㉞	㉞	—	—	—	—
	㉟	—	—	—	—
㉟	㉟	—	—	—	—
	㊱	—	—	—	—
㊱	㊱	—	—	—	—
	㊲	—	—	—	—
㊲	㊲	—	—	—	—
	㊳	—	—	—	—
㊳	㊳	—	—	—	—
	㊴	—	—	—	—
㊴	㊴	—	—	—	—
	㊵	—	—	—	—
㊵	㊵	—	—	—	—
	㊶	—	—	—	—
㊶	㊶	—	—	—	—
	㊷	—	—	—	—
㊷	㊷	—	—	—	—
	㊸	—	—	—	—
㊸	㊸	—	—	—	—
	㊹	—	—	—	—
㊹	㊹	—	—	—	—
	㊺	—	—	—	—
㊺	㊺	—	—	—	—
	㊻	—	—	—	—
㊻	㊻	—	—	—	—
	㊼	—	—	—	—
㊼	㊼	—	—	—	—
	㊽	—	—	—	—
㊽	㊽	—	—	—	—
	㊾	—	—	—	—
㊾	㊾	—	—	—	—
	㊿	—	—	—	—
㊿	㊿	—	—	—	—
	1	—	—	—	—
1	2	—	—	—	—
	3	—	—	—	—
2	4	—	—	—	—
	5	—	—	—	—
3	6	—	—	—	—
	7	—	—	—	—
4	8	—	—	—	—
	9	—	—	—	—
5	10	—	—	—	—
	11	—	—	—	—
6	12	—	—	—	—
	13	—	—	—	—
7	14	—	—	—	—
	15	—	—	—	—
8	16	—	—	—	—
	17	—	—	—	—
9	18	—	—	—	—
	19	—	—	—	—
10	20	—	—	—	—
	21	—	—	—	—
11	22	—	—	—	—
	23	—	—	—	—
12	24	—	—	—	—
	25	—	—	—	—
13	26	—	—	—	—
	27	—	—	—	—
14	28	—	—	—	—
	29	—	—	—	—
15	30	—	—	—	—
	31	—	—	—	—
16	32	—	—	—	—
	33	—	—	—	—
17	34	—	—	—	—
	35	—	—	—	—
18	36	—	—	—	—
	37	—	—	—	—
19	38	—	—	—	—
	39	—	—	—	—
20	40	—	—	—	—
	41	—	—	—	—
21	42	—	—	—	—
	43	—	—	—	—
22	44	—	—	—	—
	45	—	—	—	—
23	46	—	—	—	—
	47	—	—	—	—
24	48	—	—	—	—
	49	—	—	—	—
25	50	—	—	—	—
	51	—	—	—	—
26	52	—	—	—	—
	53	—	—	—	—
27	54	—	—	—	—
	55	—	—	—	—
28	56	—	—	—	—
	57	—	—	—	—
29	58	—	—	—	—
	59	—	—	—	—
30	60	—	—	—	—
	61	—	—	—	—
31	62	—	—	—	—
	63	—	—	—	—
32	64	—	—	—	—
	65	—	—	—	—
33	66	—	—	—	—
	67	—	—	—	—
34	68	—	—	—	—
	69	—	—	—	—
35	70	—	—	—	—
	71	—	—	—	—
36	72	—	—	—	—
	73	—	—	—	—
37	74	—	—	—	—
	75	—	—	—	—
38	76	—	—	—	—
	77	—	—	—	—
39	78	—	—	—	—
	79	—	—	—	—
40	80	—	—	—	—
	81	—	—	—	—
41	82	—	—	—	—
	83	—	—	—	—
42	84	—	—	—	—
	85	—	—	—	—
43	86	—	—	—	—
	87	—	—	—	—
44	88	—	—	—	—
	89	—	—	—	—
45	90	—	—	—	—
	91	—	—	—	—
46	92	—	—	—	—
	93	—	—	—	—
47	94	—	—	—	—
	95	—	—	—	—
48	96	—	—	—	—
	97	—	—	—	—
49	98	—	—	—	—
	99	—	—	—	—
50	100	—	—	—	—
	101	—	—	—	—
51	102	—	—	—	—
	103	—	—	—	—
52	104	—	—	—	—
	105	—	—	—	—
53	106	—	—	—	—
	107	—	—	—	—
54	108	—	—	—	—
	109	—	—	—	—
55	110	—	—	—	—
	111	—	—	—	—
56	112	—	—	—	—
	113	—	—	—	—
57	114	—	—	—	—
	115	—	—	—	—
58	116	—	—	—	—
	117	—	—	—	—
59	118	—	—	—	—
	119	—	—	—	—
60	120	—	—	—	—
	121	—	—	—	—
61	122	—	—	—	—
	123	—	—	—	—
62	124	—	—	—	—
	125	—	—	—	—
63	126	—	—	—	—
	127	—	—	—	—
64	128	—	—	—	—
	129	—	—	—	—
65	130	—	—	—	—
	131	—	—	—	—
66	132	—	—	—	—
	133	—	—	—	—
67	134	—	—	—	—
	135	—	—	—	—
68	136	—	—	—	—
	137	—	—	—	—
69	138	—	—	—	—
	139	—	—	—	—
70	140	—	—	—	—
	141	—	—	—	—
71	142	—	—	—	—
	143	—	—	—	—
72	144	—	—	—	—
	145	—	—	—	—
73	146	—	—	—	—
	147	—	—	—	—
74	148	—	—	—	—
	149	—	—	—	—

excellent thixotropy, and moreover their storage stability and the workability at the time of mixing and application are excellent; therefore they bond strongly to substrates such as primer-treated metals, concrete, mortar, wood, plastics, etc., thus they can be effectively utilized in uses such as sealants, fillers, adhesives, etc.



L8 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2002 ACS  
 AN 1985:561385 CAPLUS  
 DN 103:161385  
 TI Thixotropic polyurethane compositions  
 PA Yokohama Rubber Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 4 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C08L075-04  
 ICS C08K003-36; C08K005-21  
 ICA C09D003-72; C09J003-16; C09K003-10  
 CC 37-6 (Plastics Manufacture and Processing)  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 60120750	A2	19850628	JP 1983-226738	19831202 <--
	JP 62044784	B4	19870922		
AB	Title compns. with good storage stability, useful as sealants, gap fillers, and adhesives (no data), comprise polyurethanes 100, urea derivs. 0.1-20, and colloidal silica 0.1-50 parts. Thus, polyoxypropylene triol (mol. wt. 5000) 56, poly(propylene glycol) (mol. wt. 2000) 44, DOP 20, and MDI 20 parts were stirred at 80.degree. under N to obtain a urethane prepolymer contg. 2.54% free NCO, 100 parts of which was mixed with DOP 60, CaCO3 50, Aerosil (colloidal silica) 10, and tetramethylurea (I) [632-22-4] 3 parts, and kneaded at room temp. to obtain a paste-like polyurethane compn. with good thixotropy (JIS A 5758 sealant slumping test). Compns. prepd. similarly without the Aerosil or I showed no thixotropy.				
ST	thixotropic polyurethane silica urea deriv; sealant slumping resistant thixotropic polyurethane; sagging resistant sealant thixotropic polyurethane; methylurea colloidal silica thixotropic polyurethane; colloidal silica tetramethylurea thixotropic polyurethane; urethane polymer compn thixotropic				
IT	Urethane polymers, uses and miscellaneous RL: USES (Uses) (mixts. with colloidal silica and urea derivs., thixotropic, storage-stable, for sealants and adhesives)				
IT	Thixotropic substances (polyurethanes contg. colloidal silica and urea derivs., storage-stable, for sagging-resistant sealants and adhesives)				
IT	Sealing compositions (sagging-resistant, polyurethanes for, contg. colloidal silica and urea derivs., thixotropic, storage-stable)				
IT	Amides, uses and miscellaneous RL: USES (Uses) (amino, polyurethane compns. contg., with colloidal silica, thixotropic, storage-stable, for sagging-resistant sealants and adhesives)				
IT	7631-86-9, uses and miscellaneous RL: USES (Uses) (colloidal, polyurethane compns. contg., with urea derivs., thixotropic, storage-stable, for sagging-resistant sealants and adhesives)				
IT	101-68-8D, polymers with poly(propylene glycol) and polyoxypropylene triols 25322-69-4D, polymers with polyoxypropylene triols and MDI 25322-69-4D, triol derivs., polymers with poly(propylene glycol) and MDI RL: USES (Uses) (mixts. with colloidal silica and urea derivs., thixotropic, storage-stable, for sealants and adhesives)				

IT 80-73-9 632-22-4 1187-03-7

RL: USES (Uses)

(polyurethane compns. contg., with colloidal silica, thixotropic, storage-stable, for sagging-resistant sealants and adhesives)

RN 7631-86-9

RN 101-68-8D

RN 25322-69-4D

RN 25322-69-4D

RN 80-73-9

RN 632-22-4

RN 1187-03-7

L8 ANSWER 2 OF 3 WPIDS (C) 2002 THOMSON DERWENT

AN 1985-193504 [32] WPIDS

DNC C1985-084377

TI Thixotropic polyurethane compsn. - contains urea deriv. and colloidal silica.

DC A25

PA (YOKO) YOKOHAMA RUBBER CO LTD

CYC 1

PI JP 60120750 A 19850628 (198532)\* 4p <--

JP 62044784 B 19870922 (198741)

ADT JP 60120750 A JP 1983-226738 19831202

PRAI JP 1983-226738 19831202

IC C08K003-36; C08K005-21; C08L075-04; C09D003-72; C09J003-16; C09K003-10

AB JP 60120750 A UPAB: 19930925

Polyurethane compsn. with thixotropy contains 100 pts. wt. of polyurethane resin, 0.1-20 pts. wt. of urea deriv. and 0.1-50 pts. wt. of colloidal silica.

Pref. the polyurethane resin of a single component type is a polyurethane prepolymer contg. a terminal isocyanate gp. The prepolymer is prepd. by reacting polyether polyol or polyols contg. a terminal hydroxyl gp. having an average mol. wt. of 1000-10000 with polyisocyanates. The polyurethane resin of a two-component type is composed of a prepolymer contg. a terminal hydroxyl gp. having an average mol. wt. of 1000-5000. The urea deriv. is e.g., tetramethyl urea, tetraethyl urea and 1,3-dimethyl-2-imidazoline. The colloidal silica is e.g., aerosol.

USE/ADVANTAGE - The polyurethane compsn. is superior in heat resistance, weather resistance without redn. in storage stability and workability, and is useful for a sealing material, filler and adhesive. 0/0

FS CPI

FA AB

MC CPI: A05-G01B; A08-M06; A08-R06; A12-A05F; A12-R08

L8 ANSWER 3 OF 3 JAPIO COPYRIGHT 2002 JPO

AN 1985-120750 JAPIO

TI THIXOTROPIC POLYURETHANE COMPOSITION

IN SHIN NORIAKI; KITAMURA TETSUJI; NAKAUSA RIYUUICHI

PA YOKOHAMA RUBBER CO LTD:THE, JP (CO 000671)

PI JP 60120750 A 19850628 Showa

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IC ICM (4) C08L075-04

ICS (4) C08K003-36; (4) C08K005-21

ICA (4) C09D003-72; (4) C09J003-16; (4) C09K003-10

AB PURPOSE: To provide a compsn. having thixotropic properties without lowering storage stability, workability such as blending, or application, by incorporating a polyurethane resin with a urea deriv. and colloidal silica.

CONSTITUTION: 0.1-20pts.wt. urea deriv. (e.g., tetramethylurea) (B) and

0.1- 50pts.wt. colloidal silica (C) are incorporated with 100pts.wt. polyurethane resin (A) to yield the titled compsn. So far, it has been proposed that by incorporating component C into component A, thixotropic properties are imparted and sagging during application is prevented. However, an increase in the amount of anti-sag agent has a defect that the viscosity of resin is increased and workability is lowered, and also tends to increase the hardness and modulus and decrease the elongation and adhesion. By further adding component B, proper thixotropic properties are imparted and other properties required for polyurethane, such as workability during blending and application, are maintained sufficiently.

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☐ 1. Document ID: JP 60120750 A

L1: Entry 1 of 2

File: JPAB

Jun 28, 1985

PUB-NO: JP360120750A

DOCUMENT-IDENTIFIER: JP 60120750 A

TITLE: THIXOTROPIC POLYURETHANE COMPOSITION

PUBN-DATE: June 28, 1985

## INVENTOR-INFORMATION:

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YOKOHAMA RUBBER CO LTD:THE

APPL-NO: JP58226738

APPL-DATE: December 2, 1983

US-CL-CURRENT: 524/59

INT-CL (IPC): C08L 75/04; C08K 3/36; C08K 5/21; C09D 3/72; C09J 3/16; C09K 3/10

## ABSTRACT:

PURPOSE: To provide a compsn. having thixotropic properties without lowering storage stability, workability such as blending, or application, by incorporating a polyurethane resin with a urea deriv. and colloidal silica.

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Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	RMC
Drawn Desc	Image										

☐ 2. Document ID: JP 60120750 A, JP 87044784 B

L1: Entry 2 of 2

File: DWPI

Jun 28, 1985

DERWENT-ACC-NO: 1985-193504  
DERWENT-WEEK: 198532  
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TITLE: Thixotropic polyurethane compsn. - contains urea deriv. and colloidal silica

PATENT-ASSIGNEE:

ASSIGNEE

YOKOHAMA RUBBER CO LTD

CODE

YOKO

PRIORITY-DATA: 1983JP-0226738 (December 2, 1983)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 60120750 A	June 28, 1985		004	
JP 87044784 B	September 22, 1987		000	

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
JP60120750A	December 2, 1983	1983JP-0226738	

INT-CL (IPC): C08K 3/36; C08K 5/21; C08L 75/04; C09D 3/72; C09J 3/16; C09K 3/10

ABSTRACTED-PUB-NO: JP60120750A

BASIC-ABSTRACT:

Polyurethane compsn. with thixotropy contains 100 pts. wt. of polyurethane resin, 0.1-20 pts. wt. of urea deriv. and 0.1-50 pts. wt. of colloidal silica.

Pref. the polyurethane resin of a single component type is a polyurethane prepolymer contg. a terminal isocyanate gp. The prepolymer is prepd. by reacting polyether polyol or polyols contg. a terminal hydroxyl gp. having an average mol. wt. of 1000-10000 with polyisocyanates. The polyurethane resin of a two-component type is composed of a prepolymer contg. a terminal hydroxyl gp. having an average mol. wt. of 1000-5000. The urea deriv. is e.g., tetramethyl urea, tetraethyl urea and 1,3-dimethyl-2-imidazoline. The colloidal silica is e.g., aerosol.

USE/ADVANTAGE - The polyurethane compsn. is superior in heat resistance, weather resistance without redn. in storage stability and workability, and is useful for a sealing material, filler and adhesive.

CHOSEN-DRAWING: Dwg.0/0

TI TLE-TERMS: THIXOTROPIC POLYURETHANE COMPOSITION CONTAIN UREA DERIVATIVE COLLOID SILICA

DERWENT-CLASS: A25

CPI-CODES: A05-G01B; A08-M06; A08-R06; A12-A05F; A12-R08;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1694U

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0034 0205 0226 1294 1297 3185 1758 2152 2218 2239 2267 2270 2282 2566 2572 2585 2600 2605 2682 2686

Multipunch Codes: 014 02& 150 209 229 240 273 308 310 329 331 338 339 340 344 346 50& 51- 512 515 532 536 541 543 575 583 589 609 721

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1985-084377

**THIXOTROPIC POLYURETHANE COMPOSITION**

Patent Number: JP60120750  
Publication date: 1985-06-28  
Inventor(s): SHIN NORIAKI; others: 02  
Applicant(s): YOKOHAMA GOMU KK  
Requested Patent: ☐ JP60120750  
Application Number: JP19830226738 19831202  
Priority Number(s):  
IPC Classification: C08L75/04; C08K3/36; C08K5/21  
EC Classification:  
Equivalents: JP1433690C, JP62044784B

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**Abstract**

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**PURPOSE:** To provide a compsn. having thixotropic properties without lowering storage stability, workability such as blending, or application, by incorporating a polyurethane resin with a urea deriv. and colloidal silica. **CONSTITUTION:** 0.1-20pts.wt. urea deriv. (e.g., tetramethylurea) (B) and 0.1- 50pts.wt. colloidal silica (C) are incorporated with 100pts.wt. polyurethane resin (A) to yield the titled compsn. So far, it has been proposed that by incorporating component C into component A, thixotropic properties are imported and sagging during application is prevented. However, an increase in the amount of anti-sag agent has a defect that the viscosity of resin is increased and workability is lowered, and also tends to increase the hardness and modulus and decrease the elongation and adhesion. By further adding component B, proper thixotropic properties are imparted and other properties required for polyurethane, such as workability during blending and application, are maintained sufficiently.

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⑨ 日本国特許庁(JP)

⑪ 特許出願公開

⑫ 公開特許公報(A)

昭60-120750

⑤ Int. Cl. <sup>4</sup>	識別記号	庁内整理番号	⑬ 公開 昭和60年(1985)6月28日
C 08 L 75/04		7019-4J	
C 08 K 3/36	CAM	6681-4J	
5/21	CAM		
// C 09 D 3/72		6516-4J	
C 09 J 3/16		7102-4J	
C 09 K 3/10		Z-6956-4H	審査請求 未請求 発明の数 1 (全4頁)

⑭ 発明の名称 揺変性ポリウレタン組成物

⑯ 特 願 昭58-226738

⑰ 出 願 昭58(1983)12月2日

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## 明 細 書

## 1. 発明の名称

揺変性ポリウレタン組成物

## 2. 特許請求の範囲

1. ポリウレタン樹脂 100重量部に対し、尿素誘導体 0.1~20重量部、コロイド状シリカ 0.1~50重量部を配合したことを特徴とする揺変性ポリウレタン組成物。

## 3. 発明の詳細な説明

本発明は、揺変性ポリウレタン組成物に関し、さらに詳しくは、ポリウレタン樹脂に尿素誘導体およびコロイド状シリカを特定量配合することにより、貯蔵安定性、混合、施工等の作業性を低下させることなく、揺変性を付与する揺変性ポリウレタン組成物に関する。

ポリウレタンはゴム弾性、耐候性、耐摩耗性等の諸特性に優れることから、エラストマー、紙、布等のコーティング材、塗料、シーリング材、接着剤、床材、壁材等の建築材料や土木材料等の広範な分野で利用されている。

このポリウレタンの施工には、一般には液状または溶液状のポリウレタンプレポリマーから成るペースト状または液状組成物が使用され、これにタルク、カーボンブラック等の充填剤や可塑剤、接着付与剤、硬化触媒、着色剤等の各種配合剤が配合される。またポリウレタンはその硬化方法によって、ウレタンプレポリマーの末端にイソシアネート基を有し、施工後大気中の水分等で硬化する一液型ポリウレタンとポリオール類で硬化する二液型とに大別される。このポリウレタンはその用途によっては施工上の点から揺変性(チキソロピー)を有することが望ましい場合が多く、例えばポリウレタンを塗料やシーリング材として垂直面に施工する場合には、ハケさばきやヘラさばきが長いため垂れ難く、仕上りも美しくなる。また、接着剤やコーティング材として多孔質の紙、布上に塗布される場合は滲み込みが少なく、塗布操作が容易となる利点がある。

このポリウレタンに揺変性を付与し、施工時の垂れを防止する一つの方法として、コロイド状シ

リカやベントナイト等の垂れ防止剤を配合することが従来より提案されている。しかし、このコロイド状シリカ等の垂れ防止剤の増量に伴って、揺変性は向上し垂れ現象を抑制するが、ポリウレタンの見掛けの粘度が著しく高くなり、混合、施工等の作業性が悪化するという欠点があり、さらには硬化後の物性においても、硬さやモジュラスが増加し、また伸張性や接着性等が低下するためシーリング材、接着剤、コーティング材等の建築材料や土木材料に要求される諸特性を満足することができない。

このように他の諸特性を損わずに揺変性を付与する方法が、種々提案されている。例えば、

①ポリウレタンポリマーにポリエチレングリコールまたはその誘導体およびコロイド状シリカを特定量混合したポリウレタン組成物(特公開45-41110号)、

②末端にイソシアネート基を有する液状ポリウレタンに無機質充填剤、ポリオキシアルキレン化合物等を配合したポリウレタン組成物(特公開47

-7632号)、

③ポリウレタン原料に、スルホキシド類等の特定の垂れ防止剤を組合わせて配合するウレタンシーリング材の製造法(特公開49-27418号)、等である。しかし、これらの方法においても未だに十分に揺変性は付与されず、貯蔵中に揺変性が変化したり、見かけ粘度が高くなるために、混合施工時の作業性が悪化するという問題は十分に解決されてはいない。

本発明は、上述の従来技術の欠点を解決すべくなされたもので、貯蔵安定性、混合、施工等の作業性を低下させることなく十分な揺変性を付与し、かつ耐熱性、耐候性、耐寒性の優れた揺変性ポリウレタン組成物を提供することを目的とし、特にシーリング材、目止め材、接着剤等に利用される。

本発明者らは、上記目的に沿って鋭意検討の結果、ポリウレタン樹脂に尿素誘導体とコロイド状シリカを特定量分散させることにより、ポリウレタンに十分な揺変性を付与し、かつ混合、施工時の加工性等ポリウレタンに要求される他の諸特性

も充分維持し得ることを見出し本発明に到達した。

すなわち、本発明はポリウレタン樹脂(ポリウレタンプレポリマー) 100重量部に対し、尿素誘導体 0.1~20重量部、コロイド状シリカ 0.1~50重量部を配合したことを特徴とする揺変性ポリウレタン組成物である。

本発明に使用するポリウレタン樹脂(ポリウレタンプレポリマー)としては、一液型の場合には、末端イソシアネート基のポリウレタンプレポリマーが用いられる。このプレポリマーは、例えばポリオキシプロピレンジオールあるいはトリオールのごときポリエーテルポリオールまたはその他、末端にヒドロキシル基を有する平均分子量1000~10000程度のポリオールと、ポリイソシアネート類とを反応させることにより製造される。ポリイソシアネート類としては、トリレンジイソシアネート(TDI)、4,4'-ジフェニルメタンジイソシアネート(MDI)、その他の単独あるいは組合せ、または変性したものをを用いることができ

る。一液性ポリウレタンの場合、上記プレポリマーの末端イソシアネート基が大気中の水分と反応して巨大分子あるいは網目状分子となる。これは弾性を特徴とするポリウレタンの主構造を形成する。

二液性ポリウレタンの場合のベースとなるポリマーは、上記一液性ポリウレタンと同様の末端イソシアネート基のプレポリマーを1成分とし、平均分子量1000~5000程度の末端ヒドロキシル基のポリオールを他の成分とするのが普通である。ポリオールとしてはポリオキシプロピレンジオールおよびポリオキシプロピレントリオールまたはこれらのエチレンオキシドとの共重合物を用いることが多いが、他のポリオールを用いることもできる。二液性ポリウレタンはプレポリマー成分とポリオール成分を施工直前に混合する。反応は両成分の末端基の結合すなわちウレタン結合が主であり、水分とは無関係に硬化し得る。

これらのポリウレタン樹脂は本来液状であるかまたは溶剤に溶かして液状としたものである。こ



こに用いられる溶剤としては、例えば酢酸エチル等のエステル類、メチルエチルケトン等のケトン類、トルエン等の芳香族炭化水素類等が例示される。

本発明で配合される尿素誘導体とは、例えばテトラメチルウレア、テトラエチルウレア、1,3-ジメチル-2イミダゾリドン等であり、尿素基 1個あたり分子量1000以内の化合物が好ましい。尿素誘導体の配合量はポリウレタン樹脂 100重量部に対して 0.1~20重量部、好ましくは 0.5~10重量部である。尿素誘導体の配合量が 0.1重量部未満では目的とする揺変性が得られず、垂れ防止作用が不十分であり、また 20重量部を越えると貯蔵安定性および作業性が悪くなる。

本発明で配合するコロイド状シリカは、市販されているものを適宜用いることができ、例えばエアロジル等が代表される。コロイド状シリカの配合量はポリウレタン樹脂 100重量部に対し、0.1~50重量部、好ましくは 1~15重量部である。コロイド状シリカの配合量が 0.1重量部未満では揺

変性、垂れ防止が不十分で、50重量部を越えると貯蔵安定性、作業性が悪くなる。

本発明においては、ポリウレタン樹脂に尿素誘導体とコロイド状シリカを併用して配合することによって、コロイド状シリカのシラノール基の水素結合がより促進され、連続的な構造を形成する。この構造は弱い外力によって簡単に破壊し、一時的に粘度が低下するが、外力を取り除くと連続的な構造が再現される。従って、本発明のポリウレタン組成物は、混合、施工時には流動性がよく所望部分に所望の形状を塗布することができ、かつ作業終了後には、見掛け粘度が高いために垂れ現象を抑制する。

本発明のポリウレタン組成物においては、これら必須成分に加えて、充填剤、可塑剤、硬化促進剤、接着性付与剤、硬化触媒、着色剤等を必要に応じて適量配合することもできる。

以下、本発明を実施例および比較例に基づき詳細に説明する。

#### 実施例 1~3 および 比較例 1

分子量 5000 のポリオキシプロピレントリオール 56 重量部と、分子量 2000 のポリオキシプロピレグリコール 44 重量部、ジオクチルフタレート 20 重量部を反応容器に投入し、100℃にて減圧脱水した後、窒素ガス封入のもとに 80℃に冷却した。攪拌しながら 4,4'-ジフェニルメタンジイソシアネート (MDI) を 20 重量部添加し、遊離イソシアネートが 2.54% になるまで反応させ、ウレタンプレポリマーを調製した。

乾燥窒素ガス封入の混合攪拌機中に、得られたウレタンプレポリマー、無機質充填剤、可塑剤等を第 1 表に示す通りの配合比で投入して室温で攪拌混練し、ペースト状ポリウレタン組成物を調製した。

このポリウレタン組成物を J I S A 5758 1979 建築用シーリング材スランブ試験法によりスランブテストを行ない、0~1mm までを揺変性有り、1mm 以上を揺変性無しとした。

スランブ試験結果を各配合剤量と共に第 1 表に

示す。

第 1 表

配 合	比較例 1	実施例 1	実施例 2	実施例 3
ポリウレタン樹脂	100	100	100	100
可 塑 剤 * 1	60	60	60	60
充 填 剤 * 2	50	50	50	50
コロイド状シリカ * 3	10	10	10	10
尿素誘導体-1 * 4	—	3	—	—
尿素誘導体-2 * 5	—	—	3	—
尿素誘導体-3 * 6	—	—	—	3
揺 変 性	無	有	有	有

\* 1: ジオクチルフタレート、\* 2: 炭酸カルシウム、\* 3: エアロジル、\* 4: テトラメチルウレア、\* 5: テトラエチルウレア、\* 6: 1,3-ジメチル-2イミダゾリノン。

この第 1 表の結果から明らかなように、ポリウレタン樹脂に尿素誘導体とコロイド状シリカを併用して配合したポリウレタン組成物 (実施例 1~3) は、ポリウレタン樹脂に尿素誘導体を配合せず、コロイド状シリカを配合したポリウレタン組成物 (比較例 1) に比較して、揺変性の点で優れていることが判る。

## 実施例4～6および比較例2

実施例1で得られたウレタンプレポリマーを用い、乾燥窒素ガス封入の混合撹拌機中に、ウレタンプレポリマー、無機質充填剤、可塑剤等を第2表に示す通りの配合比で投入して室温で撹拌混練し、ペースト状ポリウレタン組成物を調製した。

このポリウレタン組成物のスランプテストを実施例1と同様に行ない、その結果を各配合剤類と共に第2表に示す。

第2表

配 合	比較例2	実施例4	実施例5	実施例6
ポリウレタン樹脂	100	100	100	100
可 塑 剤 ホ1	60	60	60	60
充 填 剤 ホ2	50	50	50	50
コロイド状シリカ ホ3	—	8	15	10
尿素誘導体-1 ホ4	3	3	3	10
揺 動 性	無	有	有	有

この第2表から明らかなように、ポリウレタン樹脂にコロイド状シリカおよび尿素誘導体を実発明の範囲内で変換したポリウレタン組成物（実施

例4～6）は揺動性を有するが、ポリウレタン樹脂にコロイド状シリカを配合せず、尿素誘導体を配合したポリウレタン組成物（比較例2）は揺動性を有しない。

以上説明したように、ポリウレタン樹脂に尿素誘導体とコロイド状シリカを特定量併用して配合する本発明のポリウレタン組成物は、揺動性が良好で、しかも貯蔵安定性、混合、施工時の加工性に優れ、またこれらの特性に加えて耐熱性、耐候性、耐摩性にも優れていることから、プライマー処理された金属、コンクリート、モルタル、木材、プラスチック等の基材と強力に接着するため、シーリング材、目止め材、接着剤等の用途に有効に利用される。

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